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"TECTONICS AND THE FORMATION OF PHOSPHATE ROCK DEPOSITS"

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A. V. Kazakov

This article sets forth several conclusions, based on two geologic-genetic rules, concerning the geographic distribution of phosphate rock deposits.

In contrast to the previous formalist-biohermal theory, the author for the first time proved, and experimentally verified, that phosphate rocks were formed as the local marine deposits from the depths of ocean waters upon their transgression on the continent.

Following the example of investigators of the Mesozoic Russian platform and other territories, the author also demonstrated the conformity of all phosphate rock deposits of the commercial type to regions of tectonic depressions.

General theoretical and regional tectonics attained high levels of development in the works of A. P. Karpinskiy, A. D. Archangelskiy, M. S. Shatskiy, V. V. Belousov, and other investigators. However, the question of the formation of deposits of mineral resources in relation to tectonic conditions remained obscure for a long time. In recent years, in connection with geologic prospecting studies on the needs of

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ferrous and non-ferrous metallurgy, and also on rare elements and mineral-chemical raw materials (boron, arsenic, phosphorus, etc.), geologists came more and more to study this problem. This manifested itself most clearly in the field of petroleum and gas geology, where, on the basis of the work of I. M. Gubkin, the genetic relationship of petroleum and gas deposits to tectonics ("gas-petroleum structures") was clearly and distinctly demonstrated. If among geologists and petroleum experts there is developing both a common language and a common understanding of the role of enclosed structures, as upheavals of the anticlinal type in the formation of gas-petroleum deposits, then the question of some kind of relationship between phosphate rock deposits and tectonics, and the question of the forms this relationship takes, have not been considered.

1. GENETIC STAGES IN THE FORMATION OF PHOSPHATE ROCK DEPOSITS

All deposits of mineral resources of sedimentary origin pass through a ^{successive} ~~consecutive~~ series of genetic stages in their development; in accordance with a change of conditions they form new combinations, in equilibrium with their environment, of rock-forming minerals. From this point of view a correct theory of the origin of any sedimentary rock deposit should be considered not in the narrow framework of the operation of any one factor (genetic stage, which is in general of comparatively short duration), but in the entire aggregate of the conditions of sedimentary rock formation -- from the initial stage of sedimentation to the final stage of the formation of rock deposits.

Let us analyze in greater detail this basically important thesis in the particular case of the formation of phosphate rock deposits.

At the time when the character of the phosphate phase and the

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process of the chemosedimentation of the phosphate material of phosphate rocks were explained by us in sufficient fullness with physico-chemical studies (3,5,6,7). ~~Hypotheses concerning~~ the ultimate stages and evolution of the initial phosphate rock up through the phosphate rock concretions, strata, and deposits were still inadequately formulated. Accumulated material now permits us to make a series of new, far-reaching generalizations and conclusions in this sphere of sedimentary differentiation.

In the history of the evolution of every phosphate rock deposit several genetic stages, occurring in successive order, must be distinguished.

In the general process of the formation of phosphate rock deposits the stages are as follows:

a. Very Earliest Stage

Initial chemosedimentation of the colloidal-dispersed phosphate from the contents of the marine ocean water flowing over the shelf (zones of shallow water), simultaneously with mechanical sedimentation of terrigenous clastic material of varying quantity brought from the continent (figures 1 to 4).

As was shown by our special studies (5,6), the calcium phosphate (primary hydroxyl-apatite) which is precipitated at the same time encloses in its crystalline lattice a fluorine ion of ocean water, which generally contains around 1 milligram, per liter, ^{of} fluorine ion. The initial phosphate deposit, moreover, is transformed into colloidal fluorapatite, dispersed, together with the highly dispersed ^{hemogenic} ~~hemocheloid~~ ~~transliteration~~ ~~monopoly~~ calcite, in the solid mass of the deposit of "dead rock" of

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terrigenous waste (Figures 2 to 4).

b. Stage of Early Diagenesis.

From the moment of the entrance of the deposit into the stage of diagenesis, the initial friable sediment, being constantly covered by one new sedimentation after another, gradually retreats (submerges, as it were) into deeper levels, into the zone of diagenesis, where the original friable sediments are subjected to the complex cycle of chemical differentiation. In regard to the phosphate rock deposits which interest us here, the most important processes of early diagenesis are: formation and growth of macroconcretions (phosphorites, flint nodules, sedimentary pyrite, and others), as well as of microconcretions (fluconite grains, ferrous oolites, leptoclorites, etc.)

At the basis of the mechanism of the growth of concretions lies a general law -- the striving of the systems to diminish their surface energy by means of recrystallization into more coarse-grained appropriate phases, and the general characteristic which coarse crystals have of being less soluble in comparison with fine crystals. The Russian term, "drawing together" (concretion), rather clearly transmits the essence and mechanism of the process of the formation of concretions in the stage of early diagenesis. The original, highly dispersed phosphate particles, evenly distributed in the sedimentation stratum, are drawn together through the slimy solution to new centers of crystallization (the condensation of ground phases), and after the formation of concretions of phosphate rock the remaining dead rock is in general already significantly devoid of phosphorus. Thus, the generally Kimmeridgian-Oxford clays of the Moscow syncline contain in all only 0.05 - 0.10 percent P_2O_5 , while the original primary concretions of phosphate rock enclosed in them are enriched with up to 25 - 30 percent P_2O_5 .

Chemical differentiation of the deposit in the stage of early

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diagenesis, in instances of the highly intensive process of the original chemosedimentation of phosphate, can proceed to the formation of compact phosphate rock strata of the laminated type.

The phosphoritic slabs of Kurek, Shekifrov (Senoman), Yererevak ("Iyazan horizon"), the Upper Kamak deposit (Valentian), Kara-Tay (Middle Cambrian), and others, serve as examples of such a type.

c. Stage of Late Diagenesis.

The above-indicated diagenetic processes of intrastratified migration and transfer of the materials are basically the result of the biochemical disintegration of organic matter (detritus) buried in the sediments. This leads, on the one hand, to an increase in the carbon dioxide content (as a product of organic decomposition) in muddy waters -- a phenomenon which reduces the pH of the environment and increases the solubility and mobility of phosphates, carbonates, and other minerals. On the other hand, the products of the molecular ²partial ~~2~~ Russian word "chastichnyy" means both "molecular" and "partial" biochemical decay of organic matter sharply decrease the oxidation-reduction potential (EH) of the environment, imparting to it a restorative, oxygen-free character. Under these new conditions, strikingly different from the waters of the marine sedimentation stage, there actually develop in the deposits new, specific mineral -- siderites, sedimentary pyrite (marcasite), products of the reduction of the sulfate ion, etc.

Moreover, for each new phase-mineral there are its corresponding, specific conditions of the changing environment -- levels of EH, pH, ionic concentrations, gas pressure, etc. Depending on the depth of the submersion of the sediment and on its removal from the oxygenous zone, the character and direction of the biochemical decomposition of the buried

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organic matter (carbon dioxide, methane, hydrogen, and other fermentations) and also the scope of the experimentally measured diversities of the diagenetic environment can change for the redox ~~redox-transliteration~~^{*} potential over a wide range (from +300 millivolts to -600).

This diagenetic stage does not take place for all deposits. Thus, its development is generally slight for the sandy (well aerated) phosphate rock deposits of Kuzek, Bryansk, Aktyuba, and others; while on the other hand it is well developed for the silt-clay deposits of the Jurassic Northern Caucasus, the Mesozoic and Paleogene eastern slope of the Northern Urals, Kara-Tay, and other places.

d. The Latest Stage

In the abrasion of deposits containing phosphate rock this stage generally leads to their erosion and to an unloading of the washed-out phosphate rock concretions of varying sizes, in the form of an exposed layer of basic conglomerate. This frequently leads to the formation of commercial rock deposits. The Portland basic conglomerate of the Moscow oblast, the strata of phosphate rock conglomerate of the Bryansk Senoman stage, the phosphate rock deposits of Podolya, and the recently discovered Silurian rock deposits of the Leningrad oblast, for example, make up deposits in the form of strata of phosphoritic gravel-coquina.

e. The Stage of Epigenesis.

Finally, after the regression of the sea and the drying of the basin, the deposit comes into direct contact with the atmosphere in the last epigenetic stage of the sedimentary cycle.

The behavior of minerals formed in the deposit in its sedimentation and diagenetic stages is strikingly different in the epigenetic stage.

* [redox: abbreviation for "reduction-oxidation"]

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of the sedimentary cycle.

The behavior of minerals formed in the deposit in its sedimentation and diagenetic stages is strikingly different in the epigenetic stage. With regard to platform phosphate rocks, the initial stages of epigenesis, from a commercial point of view, must be considered a positive factor, leading to the fragillar disintegration of the "dead" cementing rock which binds together separate concretions of phosphorites. In this generally oxidizing, hydrolyzing epigenetic environment the basic mineral components of the above-mentioned dead "cement" (calcite, sedimentary pyrite, siliceous opal-chalcedony mass, aqueous aluminosilicates, siderite, etc.) are decomposed and pass over into new, stable phases, usually with an increase in its original size. Together with this process, the "cement" is decomposed and disintegrates, freeing more stable concretions of phosphate rock. This leads to a considerably easier and simpler concentration and exploitation of the phosphate ore.

Examples of this are the Bryansk and Yegorevsky phosphate rock ores (h), the peripheral zones of the Chuvash, Kinechok and other deposits.

On the other hand, the protracted stage of epigenesis in a podzolic, ground-climatic zone leads to the complete decomposition and loss in ground waters not only of the "cement", but also of the phosphate rock concretions embedded in it.

f. The Stage of Thermodynamic Metamorphism.

In phosphate rock deposits of the geosyncline type which are depressed, often to considerable depths, in the process of advanced orogenesis and interspersed with intrusions, the operations of thermodynamic metamorphism lead to a still greater transformation in the

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original appearance of the sedimentary phosphate rock. Thus, for the Middle Cambrian phosphate rock deposit of Kara-Tay (Kazakhstan), which experienced the most advanced stages of Caledonian and Variscian ^{sk}Variskiy - transliteration/ orogenesis, the work of P. L. Bezrukov and A. G. Trushacheva shows the following:

1. Conversion of the sedimentary phosphate rocks into crystalline "stratified apatites" (Figures 5 to 7).
2. Conversion of dolomite into diopside, serpentine, and talcum; conversion of calcite into epidote.
3. Hydrothermal processes -- occurrence of chalcopyrite, realgarite, fluorite, oscovite, with quartz, etc. are detected near the granite intrusions in the phosphate rock strata.

Striking features of the metamorphism of sedimentary phosphate rocks have been disclosed in recent years by the labors of the State Institute of Mining and Chemical Raw Materials in the territory of the Siberian platform (Silurian basin of the Lena River, Cambrian Eastern Sayansk Mountains).

The above-mentioned "genetic stages" of the formations of phosphate rock deposits have a more general importance and, as processes, apply essentially to all deposits of mineral resources of sedimentary origin, reflecting in each genetic stage of the evolution of the deposit their specific characteristics and peculiarities (for example, the series of iron ore deposits, etc.).

2. LOCALIZATION OF PHOSPHATE ROCK DEPOSITS OF THE RUSSIAN PLATFORM

The Mesozoic deposits of the Russian platform and of the Moscow syncline, which enter into the composition of the platform, have been rather fully studied in the numerous works of Soviet geologists, from

* [Variskian is a pseudo-latinized transliteration of the Russian 'Variskiy', on the analogy of many common geological adjectives formed from place names.]

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the stratigraphic, as well as the geotectonic, point of view. In recent years, in connection with the construction of deep supporting oil wells, petroleum experts have introduced much valuable factual data. All this, against the background of previously published, detailed regional structural maps, which often include isopachytes, structure contours of contacts, phase index cards, and paleogeographic diagrams, has permitted us to refine our conceptions regarding the paleotopography of the Mesozoic deposits of the platform. On the other hand, the extensive study conducted by us of the lithology of the Mesozoic deposits on the borders of the Moscow syncline has also permitted us to define more precisely the topographic character of the deposits which developed here along the separate, stratified levels of the Upper Jurassic and Lower Cretaceous (Figure 6). All this has provided a suitable basis for explaining the mechanisms involved in the localization of phosphate rock deposits, their nature, productivity, magnitude, etc. -- all in interrelation with paleotopography, that is, in the final analysis, with regional geotectonics.

If one examines the localization of our platform phosphate rock deposits, he is struck by a basic pattern -- their conformity, in a structural sense, to the main zones of depression -- to synclines, sags, and troughs, which opened into an ocean basin. Thus, the numerous platform phosphate rock deposits of the commercial type (the Upper Kama, Kostroma, Tatar and Chuvash ASSR, Ulianovsk Volga region, Moscow district, and Saratov-Syzran Volga regions) proved in their formation to be subordinate essentially to the general structural plan of development and stabilization of the Moscow syncline, which opened into the Northern Arctic Ocean (the region of the Pechora Sea and the mouths of the Pechora River).

This is clearly shown in the paleogeographic map of A. N. Mazarovich (8) for the Callovian and Oxford stages of the Russian platform

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(Figure 11), on the maps of A. D. Archangelskiy and A. N. Kozanov for the Portland and Aquilon, and others.

Turning to the Senonian phosphate rock deposits of the European part of the USSR, we observe that almost all of them are subordinate, in a structural sense, to the Dnepr-Donets (Ukrainian) trough (Kursk, Shchegry, Bryansk, Voronezh, and others), which, via the lower Volga and the Caspian Depression, is connected with the orogenic basins of Central Asia and with the Pacific Ocean -- Tethys.

An analogous pattern and conformity of the formation of phosphate rock deposits to the contours of structural depressions which opened into the ocean can be observed also in the case of a whole series of other deposits (Paleogene phosphate rocks of the Turroevian Straits, the Mesozoic phosphorites of the Lena-Vilyusky depression, the Selejuk phosphate rocks in the peripheries of the Western Ural submontane depression, the phosphate rocks of Kara-Tau, etc.).

3. THE MOSCOW SYNCLINE AND PHOSPHATE ROCK DEPOSITS

An analysis of the actual data on the distribution of phosphate rock deposits in the structural outlines of the Moscow syncline, and the geologic age of the main stages of the development of these deposits are shown in composite Table I.

From this table of the physical and geologic-age distribution of the Mesozoic phosphate rock formation along the structure of the Moscow syncline, the following conclusions ensue:

1. Geologic Age

As has now been made clear, the geologic period of the formation of all these phosphate rock deposits corresponded not to any one particular

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moment in the history of the development of this tremendous syncline, but rather to a series of consecutive and orderly geologic stages in the development of the structure itself as a whole as well as of the phosphate rock deposits associated with it.

This tremendous Mesozoic marine sedimentary cycle of the Moscow syncline, which led in its sedimentary differentiation to the development of phosphate rocks and to the formation of phosphate rock deposits, had already begun in the early stages of the Upper Jurassic sedimentary cycle (Callovia-Oxford), and a clear "phosphorite" continuation of it is detected in this structure in the Valentinian of the Lower Cretaceous.

And so, for example, for the region of the Moscow syncline the stage of the original chemosedimentation of phosphate and the diagenetic phase of the formation of initial, indigenous phosphoritic concretions extended over a long period of time -- from the Lower Callovian to the Valentinian, inclusively. The principal stages of the erosive formation of the "phosphorite strata" (rock deposits), however, correspond to comparatively short moments in geologic history -- to the century of the Portland zone of the Valentinian, and also to the beginning stages of the Lower Cretaceous, when, as a result of large-scale transgressions, phosphorite-bearing Upper Jurassic sediments were hollowed out and the original, indigenous phosphorites confined in them changed into newly-formed phosphate rock strata in the form of basic conglomerate.

2. Synclines as Lines of Transportation for the Supply of Oceanic Phosphate Water Masses to the Platform

The early stages of the formation of phosphate rocks on the boundaries of the Moscow Syncline correspond to the highest point in the

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transgression of the Jurassic seas. These Upper Jurassic deposits are localized at the farthest distance from the Arctic Ocean -- the seat of the transgression on the Russian platform and the source of the mobile phosphates.

On the other hand, the very latest stages in the intensive formation of phosphate rocks (Valentian) correspond to the curtailment of the general transgression, and the rich, phosphorite nodular-stratified deposits of the Neocomian stage of the Moscow syncline are localized at the greatest proximity to the oceanic coastline -- the basin of the Syzola and Vychegda rivers, and of the Upper Kama, Vyatka, and Pechora.

The regions to the south, far removed from the Arctic Ocean (the basic source of the soluble mobile phosphates for the whole northeastern Russian platform), lose their phosphate-rock development in the Neocomian, either passing over into coarse, sandy deposits which are deprived of phosphorite from the practical point of view (basin of the upper Volga, the Moscow and Vladimir Oblasts), or forming pebbly phosphate rock strata of the basic conglomerate type (at the expense of the earlier-formed phosphate rock concretions of, for example, the Penza Oblast, etc.).

Thus open, ocean-communicating synclines, as one of the forms of platform, extensively developed, tectonic structures, should, as far as the formation of phosphate rocks is concerned, be considered basic routes of transportation for the migration of oceanic, phosphatized water masses to platforms, with subsequent unloading (crystallization) of dissolved phosphates along the shelves of these synclines.

3. Intraformational Anticlinal Uplifts

Right here it is necessary to take into consideration the importance of intraformational (on the borders of synclines) tectonic anticlinal uplifts for phosphate rock formation. In petroleum geology these positive structures, which facilitate the accumulation in a roof of

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petroleum and gas vaults, usually serve as an object of intensive investigation for the purpose of subsequent drilling. The experience of phosphate geology leads rather to an opposite conclusion.

Along all known platform synclines (the Moscow, Dniepr-Donets, Ulianov-Saratov with its Vatlush depression, the northern limits of the Caspian depression with the Leriz depression), phosphate rock deposits have developed to a greater or lesser degree. On the other hand, in all known platform, intraformational, regional, anticlinal uplifts we generally encounter an attenuation of phosphate rock development, and even its complete cessation as a marine chemosedimentary process. As examples of this we may cite the Vyatka elevations, the Saratov-Penza elevations, the Alstyr-Gorskly elevations in the upper reaches of the Unzha River (Kolopriv-Soligalich), the elevations along the southwestern and southeastern boundaries of the Kinesha trough, the Sviyazhsk-Tetyush elevation along the northern frontier of the Ulianov-Saratov syncline, and others.

h. Axial Zones of Synclines

The best conditions for phosphate rock development are those associated with the specific topographic zones of a shelf (zones of shallow water), where there occurs a thickening of the phosphate from the ocean water flowing over the shelf. In the deeper parts of synclines, filled with silt-pelite sediments (their axial portions, etc.), conditions for the thickening of phosphate are unfavorable. An example of this may be furnished by the phosphate-free deposits of the Oxford-Kimmeridgian calcareous clays of the series in the southern and middle portions of the Moscow syncline; while their peripheral zones—zones of shallower water—are significantly phosphatized. The same thing occurs in the case of

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the Senoman phosphates of the Dnepr-Donets depression, where in the axial portion of the structure (a gap in the Sharkov river) there is a thinning-out of the phosphorite layer, while in the peripheral northern zones (Bryansk, Zhidra) the Senoman phosphate rock stratum is developed to its maximum magnitude.

4. ROLE OF TRANSGRESSIONS AND REGRESSIONS

In the foregoing account we have noticed the role of transgressions as a factor in abrasive processes and in the formation of "phosphate layers of the conglomerate type."

However, it would be incorrect to reduce the entire significance of transgressions in the matter of phosphate rock development exclusively to the mechanical abrasive activity, with the formation of fundamental basic conglomerate. As has already been noted above, the sagging and formation of synclines (open to an ocean basin) constitute the principal act producing the displacement of ocean waters along the syncline to the platforms. Therefore, the very dynamics of ocean waters (transgression), the rising-up of the deepest currents, is the direct, the fundamentally important result of platform tectonics. In regressions we see the processes of a reverse order: one or another intraformational elevation on the boundaries of synclines brings about the reverse transfer of water masses to the ocean -- it brings about shoaling. Chances for the development of phosphate rocks under these conditions are extremely diminished. A striking example of this is the Gotaliv-Barrem stage (which followed the Valentian transgression) of the Russian platform, with their deposits of phosphate.

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5. GRANOMETRIC ANALYSIS OF DEPOSITS "BY THE QUARTZ METHOD" (PALEONOSCAPHIC METHOD OF THE RECONSTRUCTION OF PALEORELIEF)

The most intimate relation among tectonic factors, the formation of paleorelief (synclines, intraformational elevations of an anticlinal structure, and others) and the localization of phosphate rock deposits is traced more fundamentally and manifests itself in the uniformity of the relationship between the granometric composition of the terrigenous components of phosphate rocks and the containing rocks, on the one hand, and their mineralogical and chemical composition, on the other. The quality of phosphate rocks depends on details of paleorelief; that is, all things considered, on platform tectonics (chiefly).

With this aim we have worked out a special method applicable to phosphate rocks -- a granometric analysis by quartz.

The essence of the method consists of the following. A deposit is subjected in a special way to consecutive treatment by aqua regia and a solution of sodium hydroxide for the complete removal of all diagenetic products and the preservation in the rinsed "insoluble residue" only of stable elastic granules (granules of quartz, mainly). The resulting "soluble residue", after hydraulic and screen classification according to the grade of the granules and after determining the percentage of yields by fractions, is converted into an "average median of quartz" in microns for the granometric characteristic of the given deposit by means of a single figure. It was found that in all cases the peripheral, usually raised, portions of the phosphate rock deposits of the Jurassic and Lower Cretaceous periods on the Russian platform reveal one and the same direction of phase change.

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Thus, in these raised zones in the paleorelief of the peripheral portions of rock deposits, for phosphate rocks of the argillaceous type of the Mesozoic platform (Vyatka, Kineshma, Chuvashya, etc.), in addition to an increase in the size of quartz granules (in their average median = 2 microns), there are observed in the sediments the appearance of glauconite, or relative increase in the percentage of the glauconite content, a reduction in the amount of P_2O_5 , and an increase in the insoluble residue and percentage of Al_2O_3 and FeO_3 . With the further rise in paleorelief (the shoaling of a basin) granules of glauconite are converted into the ferrous glauconite type, and, finally, into ferrous oolites, or ovoids. In the final analysis, the sediments pass into the phase type of ferrous, coarse-grained, slightly-phosphatized sandstones (Upper Volga region, the southern outskirts of Tyazan oblast, etc.).

As an example, in Table II we adduce our collated material illustrating the change in the granulometric composition and quality of Valentinian deposits (phosphate rocks and containing rocks) in proportion to the degree of movement from north to south along the Central Russian syncline and its intersection of the zones of intraformational uplifts of the anticlinal type.

From Table II it can be clearly seen that the removal from the Arctic Ocean southward deep into the continent, to the intersection by the Moscow syncline of the zones of intraformational uplifts, produces the general tendency of enlargement of the granulometric composition of the sediments, and also degradation in the development of phosphate rocks -- deterioration of quality and decrease of productivity. In the northern limits of the Moscow syncline (Upper Kama deposit, the basin of the Sysola, and others) the productivity and quality of the Valentinian phosphate rock stratum attain maximum proportions -- 250 kilograms per square meter P_2O_5 with an average content in concretions of 26 - 28

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percent P_2O_5 ; deposits are characterized by fine granularity (average median of quartz ≈ 60 microns); typical silt glauconite-micaaceous deposits have been developed.

In the latitude of Alkhaylov-Bryansk-Penza, Valentian deposits, overlapping the zone of uplifts, are expressed in terms of the extremely shallow coastal phase of the average and large-grained quartz-mica sands (with medians varying from 200 to 425 microns), and by the sharply attenuated development of phosphate rocks (in the district of Alkhaylov-Bryansk, around 5 kilograms per square meter, P_2O_5 for the levels sparsely scattered in the stratum of the sandy, indigenous phosphate rocks of the "krudyashchaya" [transliteration; literally means "leached"]? Still farther south, in the direction of Tula, Orel, and Bryansk, marine deposits disappear completely, being replaced by fresh water sediments of fine and average-grained, ferruginous, generally cross-bedded gravels, and sandstones with kaolin cement ("pelika"), completely devoid of any phosphatization.

The systematic modification of the phase characteristics of marine deposits (the average median of clastic granules of quartz, productivity of phosphate rock strata in kilograms per square meter P_2O_5 , percentage of the P_2O_5 content in phosphorites, etc.) is revealed more fundamentally and is reflected in the distinct regularity of the interrelations among the oxides in the sedimentary bed itself as a whole, as well as in the phosphorite strata subordinate to it. Thus as an example we shall adduce the correlative functional relation of the content of Al_2O_3 and Fe_2O_3 to the P_2O_5 content in glauconite-mica phosphate rocks of the Valentian age (Figure 8), which relation, in its turn, is the result of the influence of the paleorelief of the sea-floor of the Valentian basin of the Moscow Syncline.

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This, in particular, disproves the contention of a number of foreign scientists (Weinschenk, G. Rosenbusch, G. Schneiderhan) concerning the absence in sedimentary rocks (in contrast to magmatic) of regularities of phase paragenesis, mineralogic association, chemical relationships among oxides, etc.

False assertions of a similar kind are made, unfortunately, by some Russian scientists, too. Thus, A. N. Zavaritskiy's textbook, Introduction to the Petrography of Sedimentary Rocks (2), states: "In the modification of the chemical composition of sedimentary rocks, brought about together with the transformation from certain types to others, there do not exist clear regular patterns which we observe in igneous rocks," (page 1); and further: "The intrinsic minerals of sedimentary rocks will form mixtures among themselves, in the composition of which there are no specific rules," (page 2).

In effect, if we wish to be consistent and proceed from these positions, we would inevitably arrive at the negation of the science of the phases of sedimentary rocks and at the impossibility of making predictions of any kind regarding either the geographical distribution of deposits of mineral resources of sedimentary genesis or the regular patterns of their quality and productivity.

6. RHYTHMS OF MESOZOIC SEDIMENT-ACCUMULATION ON THE SLOPES OF THE MOSCOW SYNCLINE (BY THE METHOD OF AVERAGE MEDIAN OF QUANTILS)

The well-investigated lithologic-stratigraphic Mesozoic complex of sediments of the Moscow syncline provides the most rewarding material for the intensive study of the regular patterns in the question of sediment-accumulation rhythms, for the construction of epeirograms of

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the movements of the earth's crust in each region, and for the practice of using rhythm-diagrams for the purpose of a stratigraphic correlation of sediments.

As we know, the rhythms of sediment-accumulation are essentially a reflection of the rhythms of the vibratory movements of the earth's crust. V. V. Belousov (in 1933 and 1934) was one of the first to demonstrate that a plan of vertical movements of various indications of the earth's crust in a given region could be reconstructed with the aid of events of equal magnitudes of the synchronous sediments (isopachytes). He arrived at this conclusion by proceeding from the principle of the compensation of vibratory movements of the earth's crust by processes of accumulation and erosion. By virtue of this principle of compensation, the magnitude of deposits in this first approach to the problem is taken as equal to the size (amplitude) of the tectonic sinking of the earth's crust. Somewhat later (1949), A. N. Konev made this method more precise by replacing the magnitude of deposits with their volume (the product of the widths of the deposits by their surface area, with correction for the contraction factor). This is the so-called volume method.

Both authors, nevertheless, arrive at the conclusion that "the guiding method in the study of the history of the undulating movements of the earth's crust is the method which is based on the study of magnitudes and phases of sedimentations."

Using this two-sided premise (magnitudes and phases) as our point of departure, we have endeavored to simplify the qualitative analysis and construction of rhythm¹⁷grams.

We took as our basis, first of all, the phase appearance of the deposits, their granulometric composition in the stage of subaqueous sedi-

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mentation, when the deposit is not as yet altered by the later stage of diagenesis (the growth of micro- and macro-concretions, etc.). Thus, in the numerical phase index of the deposits one obtains their granulometric composition, which is reflected in the magnitude of the "average median of quartz" -- the elastic material of terrigenous mud carried into the sedimentary basin from the dry land, and with its continuous remashings by waves on a level "higher than the action of waves," there must occur an inevitable sorting out and redeposition of the granules of elastic material according to their size and the depths of the "area of feasible agglomeration."

The mechanical composition of a deposit at each given point of the sea floor depends upon the hydrodynamic processes (direction of sea currents, the ebb and flow of the tides, the character of the sea-swelling, etc.), which, in its turn, is the result of the topography of the sea floor and of the configurations of the shore.

In the opinion of N. V. Klenova, "on a leveled, plane subaqueous slope of a straight coastline the mechanical composition of a deposit changes gradually, in accordance with the increase in depth; gravel is replaced by muddy sand, the latter by sandy silt, etc." In other words, the granulometric composition of a deposit changes in strict proportion to depth. The flat-surfaced character of the relatively shallow, platform Mesozoic basins with their slanting relief should approximate this type, too.

And so, in the particular case of the Mesozoic deposits of the Moscow platform syncline, the granulometric composition of the sediments (average median of quartz) in their original stage of sedimentation reflects, speaking generally, the depths of the sedimentary basin. On

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this basis we have permitted ourselves to make an experiment of the construction of rhythmostrans according to granulometric indices, and to make a reconstruction of the appearance of the paleorelief of the region under study.

Regarding the territory of the central and southern sections of the Moscow syncline for the Mesozoic (Upper Jurassic and Lower Cretaceous), eight granulometric rhythms (cycles) of sediment-accumulation are clearly distinguished (Table III and Figure 9).

Of these rhythms (cycles), apart from the first and the second, the most sharply delineated (rhythms of the first order) are the Portland (zone *Virg. virgatus*) and the two Valentians ("Kyszan horizon" and Middle Valentinian), beginning for the most part with an abrasive conglomerate to phosphate rock layer. On elevated indices of paleorelief, mainly in the southern sections of the Moscow syncline, the Ocherivskiy [transliteration] rhythm begins with a basic conglomerate of phosphorite nodules belonging to generations of various ages.

The diagram (Figure 9) shows the rhythms of Mesozoic sediment-accumulation in coordinates of time (geologic indices) and granulometry of sediments ("average median of quartz" of granules of clastic minerals, in microns).

Thus, we are able to arrive at the following conclusions:

1. For the entire central and southern sections of the Moscow syncline, the elements of the rhythms (the beginning of transgression, maximum submersion and regression) coincide chronologically. This demonstrates the simultaneity of vibratory movements of one and the same kind for the entire territory of the central and southern portions of the Moscow syncline.

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2. The formation of phosphate rocks in all cases conforms to the element of rhythm which reflects the state of transgression. On the other hand, degradation of phosphate rock development corresponds to stages of regression.

3. The tectonic system of the northern boundaries of the Moscow syncline (Upper Kamsk-Synol region) differs essentially from its central and southern sections. In the Moscow region of the basin a rising-movement tendency takes place for the Neocomian; in the northern Upper Kamsk region, on the other hand, sinking and laying-down of extremely fine-grained sediments are characteristic tendencies for the same period.

4. Genetically, concretions of marl, phosphite, siderite, limonite, and others represent portions of containing rock which were cemented in the process of diagenesis by one or another material from muddy solutions. Therefore, the granulometry of quartz granules of concretions usually corresponds to the granulometry of the quartz granules of the containing rock itself. It is this phenomenon which makes for the great superiority of our method of constructing rhythmograms by the 'median-of-quartz' method. It is common knowledge that the true magnitudes of deposits are relatively rarely preserved in nature (the influence of the processes of abrasion, erosion, etc.), which fact, naturally, limits the applicability of the isopachyte method of V. V. Belousov, and, consequently, of its variant, the volume method of A. B. Ronov. However, in the case of the application of our granulometric method of constructing rhythmograms, the preservation of the full, true magnitude of deposits does not essentially have such a decisive importance. Moreover, the granulometric method is especially valuable for the reconstruction of the lithologic features of washed-away strata, of which frequently only relics in

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the form of redeposited pebbles of phosphate rock and other concretions remain.

The granulometric method of the medians of quartz proved to be highly sensitive. Thus, on the boundaries of outcrop such details as all of the three zones of the Aquilon are rather clearly rejected by this method (cf. Figure 2); in addition, the lower Fulgens zone proves to be the most fine-grained, the Katanulyat somewhat more coarse-grained in all instances, and the upper Nedigerov has the maximum median-of-quartz value.

5. The evolution of all rhythmic processes and consequently of the epirogenic movements of the earth's crust too, had a specific direction in the Upper Jurassic and partly in the Lower Cretaceous periods for the greater part of the territory of the Moscow syncline. The duration of each rhythm, the corresponding magnitudes of the deposits, and the average depth of the basins decreased with the passing of geologic time; on the other hand, the coarseness of the elastic granules and the corresponding shallowness of the basins increased. The epirogenic, vibrating movements of the earth's crust and the rate of phosphate rock development were dying out. The Jurassic-Cretaceous sedimentary megacycle was approaching its completion and coming to an end in the borders of the Moscow syncline, principally with continental deposits of apatite, before the new Upper Cretaceous, Alb-Senoman transgression.

7. GEOTECTONIC SYSTEM OF THE FORMATION OF PERMIAN

PHOSPHATE ROCK DEPOSITS OF THE USA

For a comparison of the geotectonic and general lithologic-genetic system of the phosphate rock deposits of the Russian platform with the world-wide phosphate rock deposits of foreign countries, great interest is presented by the US with its tremendous phosphate rock de-

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posits of the geosyncline type associated with deposits of the Permian age. An analysis of the great amount of factual material, charts and maps in the work of D. Condit, published in 1928 (13), permits us to make the following conclusions and generalizations.

1. The map of the localizations of phosphate rock deposits, and the isopachytes of the magnitudes of phosphate rock strata appearing with it (Figure 10), clearly show the conformity of all Permian phosphate rock deposits of the US Rocky Mountains to a vast, meridionally elongated depression of the geosyncline type, bound by zones of great regional uplifts -- on the northeast by the Canadian shield, and on the east by the Paleozoic elevations of the Appalachian mountains (orogenic zone of the Caledonian).

2. A paleogeographically reconstructed form of the ore is represented in the form of a meridionally elongated, huge flat lens with magnitudes decreasing from the central axial line (4-foot isopachyte) eastward and, apparently, westward. The southern end of this lens is not yet shown in the work of D. Condit.

3. This Permian depression of the geosyncline type in its northern end opens into the northeastern part of the Pacific Ocean and neighboring regions of the Arctic Ocean, in the state of Montana, on approximately the 110 degree to 115 degree meridian west longitude from Greenwich (the sources of the Mackenzie River, approximately 1,600 kilometers to the east of the eastern border of Alaska). Phosphate rocks are traced up to the 47 degree north latitude.

4. In an earlier published work (5) we gave, on the basis of the materials in the above-mentioned publication (13), a lithologic-phase analysis of three latitudinal profiles across the Permian phosphate formation of the geosyncline type in the US (southern profile along

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the 45 degree parallel; the central along the 45 degree; the northern along the 46 degree, 30 minute). Here we encountered patterns known to us from the Russian platform. In all instances without exception, the intersection by these profiles of zones of intraformational uplifts, or any approach to them, led to the degradation of phosphate rocks deteriorated, the phosphate rocks being converted into what is well known to us from the Russian platform -- into the quartz-clausonite, sandy, nodular type with 18 - 20 percent P_2O_5 content. Finally, still farther to the east, in proportion as it approaches the zones of the elevations of the Canadian shield (Wind River and Loner, Wyoming) the Permian phosphate phase dies out in general, being replaced by a phase of quartzite, sandstone, and flint deposits.

All that has been stated above suggests very vividly the analogous patterns for phosphate rock deposits on the Moscow syncline, reflecting in many respects the common character of the genetic nature of both, in spite of the differences in the rates of phosphate accumulation and in the geotectonic type of the respective deposits.

8. SOME CONCLUSIONS REGARDING THE DISTRIBUTION OF PHOSPHATE ROCK DEPOSITS

Scientifically substantiated predictions regarding the geographic distribution of deposits of mineral wealth in the territory of one or another country and region is one of the most urgent, and at the same time, one of the most complex problems of the geological-mineralogical sciences. Moreover, it is completely obvious that, independent of the form and type of a mineral, the basic prerequisite for a successful solution of these prognostic problems is a correct theory regarding the conditions of the genesis of an ore-forming mineral itself as well as of the circumstances of the deposit-formation of the given mineral.

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We shall review briefly these theoretic premises and generalizations on which we have built our conception of a prediction of the geographic distribution of phosphate rock deposits.

1. In contrast to past, long-held views (the biolitic theory), the formation of phosphate rocks is linked with the precipitation of highly dispersed phosphate material of a fluor-apatitic nature out of oceanic water masses (marine water of normal salinity). This basic process of initial enomocclitization of phosphate has been analyzed in detail by us in special published works and has been verified experimentally (3, 5, 6). This position eliminates from the items to be used for predictions concerning phosphate rocks the regions of continental deposits (the dry land) and also territories occupied by fresh-water and salt basins.

2. In the diagenetic process the original phosphate coagulum, dispersed in the dead rock mass (terrigenous removal), undergoes differentiation, isolating itself, in comparison with the original correspondence between the phosphate mass and the dead rock, in the form of concretions and substance of a platy-stratified texture.

3. Frequently, the subsequent abrasive processes lead to a mechanical unloading of the phosphate rocks in the form of pebbly phosphate rock strata or basic conglomerate, forming at the same time several rock deposits of the commercial type (Aktyuba, Bryansk, Yegorovsk, and others).

4. A careful study of the history of the development of the geotectonic system and of its accompanying paleogeography, and especially of paleorelief, should be the foundation of regional predictions of the geographic distribution of phosphate rock deposits.

5. On this basis the territory of the region under investigation can be subdivided for the succession of periods and ages into prospective

* [Note: The original word 'snos' has the literal meaning of 'borne off' or 'carried away', and therefore may suggest such ideas as 'detritus', 'rubble', 'waste', 'debris', etc.]

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and non-prospective regions, from the point of view of the likelihood of the occurrence of phosphate rock deposits.

To the prospective category belong zones of depression -- synclines, sagging, troughs, straits -- which opened directly into an ocean basin and which were the basic transportation routes for conveying phosphatized, deep-seated ocean water masses deep into the adjoining continent.

Geologic age does not play an essential role in the formation of these depressions, since the formation of phosphate rocks, from a world-wide point of view, has been traced in an uninterrupted sequence from the Cambrian and Proterozoic eras up to the present time. It is evident that the essential role is played by the depth of these depressions and by the absence of shoals or bars which seal off the heart of a continent to ocean waters. In accordance with the vertical distribution of the P_2O_5 , CO_2 content in ocean waters, the upper layers of water down to a depth of 50 to 100 meters offer comparatively little interest from the point of view of the thickening of calcium phosphate because of their phosphorous deficiency; on the other hand, the deeper, cold ocean waters, rich in carbon dioxide, are the basic source of mobile phosphates and in shallow water zones, under conditions of a continuous supply of ocean water (floor currents), are capable of crystallizing out rather large masses of phosphates. This limits the necessary depth of such depressions -- roughly calculated by us to around a 100-meter column of running water.

6. In accordance with the extremely slow nature of the process of phosphate rock formation, the depressed zones opening into the ocean, which interest us here, must be paleogeographically preserved (must be stable) over a protracted geologic period.

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Thus, the Moscow syncline in the period of phosphate rock formation existed in the Upper Jurassic and encroached upon part of the Lower Cretaceous (the Valentin period, so that, in absolute chronology, this corresponds to a whole epoch: J_3 -- 13 million years, and one period -- the Valentin -- approximately 4 million years; 17 million years in all).

The cordilleran geosyncline of the US existed securely for around 20 million years during the period of its Lower Permian phosphate rock formation (P_1). The submontane Western Ural depression, which predetermined the formation of the geosyncline type of Artinskian [Artinskian] Artinskian phosphate rocks (P_1), existed for around 10 million years, etc.

7. Excluded also from the prospective regions of phosphate-accumulation are depressions of the enclosed type -- hollows, intermontane cavities, grabens, continental tectonic breaks. To this same category of depressions, non-prospective for phosphate accumulation, apparently belong hollows with developed carbon accumulation and salification and, also, deposits coincident with regional paleo-uplifts of the second and third order (embankments, bosses, etc.).

Phosphate shelves should be considered above all as regions of shallow water (around 50 meters in depth), and from this point of view they are structural elements of the depressed zones themselves, usually constituting their peripheral portions (the coastal, border zones).

Without waiting for the final conclusion of previously begun summaries of the history of the development of the geotectonic system of the individual regions of Siberia, we are able at the present time, by proceeding from the above stated premises, to give several concrete examples (for the most part along the territory of the Siberian platform

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and the Western Siberian plain).

1. The Ob-Irtysh syncline along the eastern slope of the Urals (Figure 11). The labors of the past years have considerably penetrated the structural features of this extensive syncline which opened into the Arctic Ocean (the Kara Sea) as early as the Gallovian stage. Its axial zone runs almost meridionally, approximately along the Ob Bay-Tyumen River line, and is filled with thick marine deposits of the Mesozoic and Paleogene (up to 2000 meters). To the west, in the direction of the foothills of the Ural range, one observes a general rising of the sedimentary strata and their corresponding systematic phase change, progressing to the very transformation of the marine sediments into continental ones. Parallel with the above-indicated axial line of the syncline, lines of depressions, belonging to the category of the second order, are also found. For research in phosphate rock deposits, naturally only this sloping, relatively narrow zone along the eastern slope of the Urals offers a subsequent practical interest.

The phase change of deposits occurs not only in latitudinal profiles, but also meridionally (a phenomenon of the undulation of the axes of the syncline). Therefore, Mesozoic deposits (J_3 plus Cr_1) of the sloping zone along the eastern slope of the Urals, roughly southward from the latitude of Martsyata, offer little prospect for phosphate formation. Phosphorite-bearing deposits are represented for the most part by the marine Paleogene with a weakly developed phosphate rock stratum. Exploitation of this kind of phosphate rock strata can hold a practical interest only in connection with a complex exploitation of other ores.

We should prospect for Mesozoic phosphate rocks (Valentian) in the northern half of the Ob-Irtysh syncline, along the sloping eastern

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zone of the Urals. These deposits are clearly phosphatized.

2. The Mesozoic Lena-Vilyui depression of the Siberian platform, which began its development in the beginning of the Jurassic and was inundated by the sea in the Middle and Upper Jurassic, wholly completed its depressed, marine structural appearance in the Upper Cretaceous. In mesozoic times this Lena-Vilyui depression communicated with the Arctic Ocean.

This huge depression is bordered on the east and west by ancient folded structures. According to data in our possession, the phosphate rocks coincide with marine deposits of the Middle Jurassic (J_2).

3. The lower Permian "Verkhoyansk arch" of the Mesozoic-Alpine folded zone bounds the Siberian platform on the northeast and is composed of deposits P_1 plus T_1 plus T_2 of the geosyncline type.

The region of the Verkhoyansk arch in the Lower Permian made up the western marginal section of the extensive Permian-Triassic geosyncline basin which opened into the Arctic Ocean.

The schistous-silica deposits of the (schist: * [translit.]) series (P_1) of this depression are conspicuously phosphatized, and the general lithologic appearance of the deposits remind one of the phosphatized deposits of the very same age in the US. Phosphate rocks of the Permian are encountered in their own right, occurring in a thick carbonate series of deposits. Phosphatization even enters into the overlying glauconite-bearing deposits of the Triassic.

4. Silurian period of the Siberian platform. In the territory of the Siberian platform and the adjoining peripheral folded structures, the sharply increased phosphatization in deposits of the ancient Paleozoic (Silurian and Cambrian) of many regions is well known. This permits us at the present time to make a series of generalizations and prognostic conclusions.

*[Note: This word may be a Russian transliteration (in adjectival form, as indicated by the suffix -sk or -skiy) of some English word that would be spelled "witch", or from some other non-Russian word of similar sound.]

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a. The eastern, southern and southwestern peripheral zones of the Silurian field of deposits -- zones adjacent, respectively, to the Aldan and Baikal folded zones -- consist of shallow water, littoral sand deposits with sandy phosphate rocks of negligible magnitude. The phosphate rocks here are associated with the sandy-clayey series of the manyrsk [translit.] horizon S^2_1 . The commercial importance of these phosphate rocks of the peripheral-littoral zones is of little promise.

b. A different phase character is possessed by the Silurian deposits and their subordinate phosphate rocks of the northern zone. The Silurian is here represented by deeper water deposits (from siltstones to carbonaceous-calcareous strata). In conformity with this, the phosphate rocks actually discovered here in the form of exposed layers were of a higher quality.

5. Cambrian-Proterozoic. It was in very recent years (1948-1949) that information first appeared concerning the increased phosphatization along a whole series of regions which were points for deposits of the extensive Cambrian basin. The first "phosphate points" turned out to be the Sayansk and the central portion of the Siberian platform.

Not so long ago it was still the opinion of geologists that phosphate rocks were not to be found in Siberia: "Phosphate rocks in the USSR must occur almost exclusively in the Mesozoic and Paleogene deposits of the Russian platform. In Siberia they are completely unknown." (1)

Contemporary Soviet geologic science, with its theoretically developed study of the lithogenesis of sedimentary rocks and of their mineral products, and with its complex approach (geology plus chemistry) to the solution of problems, disproves this former view. Phosphate

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rocks do occur in Siberia.

In conclusion, I should like to urge geologists and lithologists to the recognition of that basic proposition of our science; namely, that without the application of contemporary methods of physical chemistry, the full disclosure and understanding of the geologic-genetic pattern, to which phosphate rock formation and the mineral products dependent on it conform, become impossible. To this category belong such urgent and immediate problems as the following:

- a. The correct interpretation of the genetic conditions and age relationships in cases of a joint occurrence in one stratum, specimen, or rock concretion of rock ores of genetically different minerals.
- b. The formation of dolomite.
- c. Sedimentary minerals -- phases of variable composition.
- d. The role of ferrous chlorites as basic concentrators of iron in the sedimentary and diagenetic stages of the formation of iron ore deposits of sedimentary origin.
- e. The problem of the formation of petroleum and combustible gases as a result of deposits of organic material, and the role in this process of thermodynamic factors. Reversible and irreversible systems.
- f. The physical chemistry and biochemistry of the processes of the diageneses of sediments in fresh water and marine basins, and the role in these processes of the oxidation-reduction potential.

I shall pause here to discuss in somewhat greater detail only the first two examples.

In recent years, in the practice of geologic-prospecting operations, there have more and more frequently been encountered cases of a concomitant occurrence in one stratum of a deposit, in one and the

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same ore specimen, and even in one concretion, of genetically heterogeneous sedimentary minerals. Thus, in Middle Jurassic deposits of the northern slope of the Caucasus, the joint presence of phosphorite and siderite in intimate mutual combination is highly developed. In the Ob-Irtysk syncline, along the eastern slope of the Urals, the mineral association phosphorite-siderite-rhodochrosite (MnCO_3) is very widely developed in Paleogene deposits. In the Middle Cambrian sediments of Kara-Tay and in the upper carboniferous deposits of the submontane depression along the western slope of the Urals, the mineral association phosphorite-dolomite is extensively developed. All these facts are generally explained by geologists on the basis of the formalist understanding of the science of paragenesis. In addition, the fact of the joint occurrence of these minerals is interpreted as due to their simultaneous formation and the common parameters of their genetic environment. Still quite recently, in a whole series of works, these minerals accompanying phosphorite (siderite, dolomite, segregations of manganic deposits) were raised to the status of "prospecting indicators" of phosphate rocks. All this confusion existed until, by methods of physical chemistry, we worked through the systems of physical-chemical equilibria for apatite, siderite and dolomite (partly) around phases. Moreover, it was found that the parameters of the formation and stability of these minerals are highly dissimilar, that they do not overlap one another, and that, consequently, it is out of the question to consider that they have a common origin or that one of them could be a prospecting indicator for another. As a consequence of this, the ground is cut from under the proposition of the "simultaneity" of the formation of these minerals of concomitant occurrence. We shall adduce here a comparative table of the basic physico-chemical parameters of the fields

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of the development and stability of these minerals studied by us and their corresponding systems (See Table IV).

In the sedimentary stage the phosphate element is precipitated in the form of a highly dispersed sediment of apatite texture, whose physico-chemical parameters of formation are close to the parameters of the deep-seated layers of the ocean water itself. Neither siderite nor dolomite can be formed in this marine sedimentary stage. In the subsequent diagenetic stage in the existence of the deposit, with the attainment in the muddy environment (water) of a level of an oxidation-reduction potential of not higher than 10 mV, conditions arise in the oxygen-free environment with a negative redox-potential for the formation of siderite (Figure 12). The process functions mostly at the expense of the transformation (reduction) of ferric compounds of the sedimentary stage into ferrous compounds, and at the expense of the presence in the "closed system" of the diagenetic muddy waters of an excess of CO_2 -- the product of the biochemical decomposition of buried organic matter. Moreover, as has already been noted, under the influence of an excess of carbon dioxide in muddy waters, there also occurs a partial ~~molecular?~~ ^{translit.} intra-layer migration of the phosphate matter deposited earlier. However, no new thickening of the additional mass of phosphate occurs in this stage, naturally.

As a preliminary hypothesis, based in part on our experimental data, we bring forth the following concept.

The decisive process in the system of mass dolomite-formation is the accumulation in a water environment (well, muddy waters) of magnesium bicarbonate, which, alone, basically ^{ensures} ~~conditions~~ both the necessary high pH and the high alkaline reserve of the environment, with the presence in the same environment of calcium bicarbonate, which

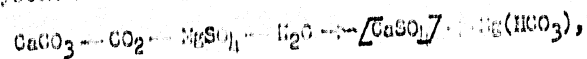
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is widely prevalent in natural waters, dolomite formation takes place, moreover, automatically.

In that way, however, can a high concentration of magnesium bicarbonate in natural systems be produced? Besides the well-known instances of the formation of dolomite in the process of atmospheric erosion and the decomposition of magnesian silicates, we may conceive of two principal ways, each of which proceeds from the magnesian salts of marine waters buried in a stratum of sediments (ancient ones, for the most part). The first way is the stoichiometrical reduction of a sulfate ion from $MgSO_4$, with the removal from the system at the same time of gaseous H_2S and the formation of magnesium bicarbonate out of the cation group and the carbon chloride of the muddy diagenetic waters.

The second way is by an interchange reaction following a modernized system of Haldinger --



which, under normal conditions of temperature and pressure, takes place very sluggishly, incompletely, and haltingly. On the other hand, according to our experimental data, under increased temperature and pressure, the course of this reaction is greatly speeded up (Figure 12). Consequently, the thermodynamic-metamorphism stage of marine deposits (especially of the geosyncline type), which partially contain calcite, in conjunction with the decomposition of buried organic matter, provides all the necessary physico-chemical prerequisites for the mass diagenetic formation of magnesium bicarbonate and calcium and, therefore, of dolomite too.

In any case, dolomite, in relation to phosphorite, is a product of very late generation and of a completely different genetic environment.

Thus, only by getting out of the narrow framework of "geologic

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experience and facts" and drawing upon the essentially different methods of physical chemistry for their interpretation, will we be able now to perceive and understand correctly the genetic nature of the above-indicated processes of sedimentary differentiation.

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Table I

LOCALIZATION OF PRINCIPAL PHOSPHATE
ROCK DEPOSITS OF THE MOSCOW SYNCLINE

Phosphate Rock Deposits of the Moscow Syncline	Geologic Age of Initial Chemosedi- mentation of Phosphate and of the Formation of Native Phosphate Rock Concretions (Stage of Diagenesis) ¹
1. Upper Kama (basins of the Kobra and Sysola)	Portland -- Aquilon -- <u>Valentian</u>
2. Kostroma in the Volga region	Callovian -- Oxford -- Kimmeridgian -- Portland -- <u>Aquilon</u> -- <u>Valentian</u>
3. Basin of the Vetluga River	Callovian -- Oxford -- Kimmeridgian -- Portland -- <u>Aquilon</u> -- <u>Valentian</u>
4. Chuvash ASSR (basins of the Sura and Pyana)	Lower Callovian -- Upper Oxford -- Kimmeridgian -- Portland -- <u>Valentian</u>
5. Tatar ASSR	Kimmeridgian -- Portland -- <u>Aquilon</u> -- <u>Valentian</u>
6. Ulyanovsk -- Syzranskoye in the Volga region	Callovian -- Oxford -- Kimmeridgian -- Portland -- <u>Aquilon</u> -- <u>Valentian</u>
7. Penza Oblast (Iybrino and others)	Callovian -- Oxford (?) -- <u>Valentian</u>
8. Moscow region	Callovian -- Oxford -- Kimmeridgian -- <u>Portland</u> -- <u>Aquilon</u> -- <u>Ryazan horizon</u>

¹The geologic age of the decisive formation of deposits, including the abrasive washout of basement strata by subsequent transgression and the unloading of phosphate rock conglomerate in the bed, is italicized.

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Table II
PHASE CHANGES ILLUSTRATING VALENTIAN DEPOSITS FROM NORTH TO SOUTH
ALONG THE MOSCOW SYNCLINE AND ITS INTERSECTION
OF ZONES OF INTERCONTINENTAL COLLISIONS

Inspection Points	Average Median of Grains of Clastic Minerals of Quartz (in microns)	Number of Points	Productivity of the Phosphorus Stratum (kg/1 m ² P ₂ O ₅)	Glauconite (in percent)	Ferric oolites	Indigenous phosphate rocks (in percent)		
						P ₂ O ₅	SiO ₂	Fe ₂ O ₃
1. Basin of the Sysola	60	--	--	--	none	26-28	10.6-7.5	3.3-4.3
2. Sources of the Kama and Vyatka	60	8	250	--	--	---	---	---
3. Southern peripheral Section	75	5	150	--	--	24-25	13-12	5.4-4.7
4. Vetluzhsko-Surskiy depression (Kurmysh)	35	5	--	--	--	17-23	---	5-6
5. Unzha River -- middle and lower course	100	5	--	--	--	18-20	30-20	20-30
6. Chuvash ASSR	38	4	--	--	--	19-21	---	8-12
7. Ul'yanovsk-Syzranskiy depression	60	3	--	--	--	---	---	---
8. Kineshma	126	3	---	no	to 30	---	---	20-30
9. Environs of Moscow	181	6	--	2	0	weak	---	---
10. Penza Oblast Mordovsk ASSR	190	4	--	no	10	17-20	35-20	5-3
11. Pronya basin	245	13	5	--	0-5	10-14		
12. Ryazan' (Novoselki)	425	6	--	--	--	12-13	70-50	3-2
13. Shatrishchi	392	--	0.5	--	tol. unit	10-14		
14. Upper Volga basin	Deposits of the Valentian were abraded by the Geterin /Geterinskiy - translit./ transgression							
15. Peripheral region of the elevation of the southern half of Tula and Ryazan Obl.	172	--	0	no	0	Region of the development of typically continental fine-grain ferrized quartz-mica sands and kaolin sandstones		

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Table III
 CHRONOSTRATIGRAPHIC CORRELATIONS OF DEPOSITS ON THE BOUNDARIES
 OF THE CENTRAL AND SOUTHERN PARTS OF THE MOSCOW SYNCLINE

Beginning of Transgression	Maximum Submerison	Regression and Partial Regression of the Sea	
		Initial Stages	Final Stages
Upper Goteriv	Upper Goteriv		Barrem
8. Sandy deposits with ferrous oolites and basic conglomerate with phosphate rocks mainly of a pebbly type	For northern de- pressed portions typical clays with early clay-siderite concretions with Stalitskites veru- beler Traut.		
7. Middle Valentin (lowest parts)	Valentin Glaconite-micaceous siltstones with phosphate rocks	Upper Valentin	
Lower Valentin (Byazan horizon)	Byazan horizon "Brown clay" in the covering of a phyllosorous stratum	Lower Valentin	
6. Glaconite-oolite ferrous sands with gravel-type phos- phate rocks, mainly of flaky texture			
Aquilon (lowest parts of zone Kash- purites vulgens Traut.)	Aquilon Zone Gr. okensis Nik. Zone Gr. sulditus Tr. Zone Gr. garnierii- coras catenulatum Fisch. Glaconite-micaceous phosphatized silt	Aquilon	Aquilon (zone Gr. nodifer
5. Glaconite-sand deposits			
Portland (zone Virgatites virga- tus)	Silt glauconite mica deposits with indigenous phosphate rocks (zone Virgatites virgatus)	Portland (strata with Nikitinella nik.) Glaconite- mica sands with conglomerate phosphorites, generally without concretions	
4. Glaconite-mica sands of trans- gression occurrence with basicphosphor- ite conglomerate			

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Table III (Continued)

GEOMETRIC RHYTHMS OF MESOZOIC DEPOSITS ON THE BOUNDARIES
OF THE CENTRAL AND SOUTHERN PORTIONS OF THE MOSCOW SYNCLINE

Beginning of Transgression	Maximum Submergence	Regression and Partial Regression of the Sea	
		Initial Stages	Final Stages
Portland (lowest parts of zone Per. panderi Etchw.	Portland (zone Per. panderi) shale series		
2. Middle (lowest parts) and Upper Callovia	Lower and Upper Oxford, Kimmeridgian Carbonaceous glauconite- mica clays	Portland (Votlyandskiy horizon), Lower Portland Volga region	
1. Bat Sandy deposits	Lower Callovian Maastrichtian siltstones	Lower Callovian	Middle Callovian
Zone Parkinsonia wurttembergica Opp.	Zone Cadomera clat- mae Nik.	Sandy deposits, strata with Koplerites ex. ex. goweri Sow.	Sandy deposits with ferro- obolite marls

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Table IV

Minerals	Fluorapatite	Siderite	Magnesite en. 165-167	Magnesite en. 75/3-75/4	Dolomite
System (Principal Components)	$\text{CaO-P}_2\text{O}_5\text{-F-H}_2\text{O}$	$\text{FeO-CO}_2\text{-H}_2\text{O}$	$\text{CaO-MgO-CO}_2\text{-H}_2\text{O}$	CaO-MgO-CO_2	$\text{CaO-MgO-CO}_2\text{-H}_2\text{O}$
Isotherm (Degrees Centigrade)	20	10-20	60	150	Lake Balkhash, Summer (N. M. Strakhov)
Equiponderant Concentra- tions of the Solutions of the System Studied (in M.L.)	From 7.0, 0.30, 16.0 To 12.0, 0.001, 1.5	Fe From 12.2 From To 26.3 CO ₂ From 116.4 to 1114.0	0-12, 08-200, 330-380	0, 126, 366	43.1, 170.? 57.0, 296.?
pH	From 8.0 to 8.5	From 6.0 to 6.5	9.14-9.43	6.74-6.87	approx. 8-9
EH (oxidation- reduction po- tential mV) ¹	Plus 500... Plus 600 (Ocean Waters on Shelf)	app. Minus 10 mV	No Direct Sig- nificance	No Direct Significance	In Baddy Waters Partial Libera- tion H ₂ S
Oxygen	Usual Oxygenous Environment of Maritime Basins	Oxygen-Free Non-Reducing Environment	No Direct Sig- nificance	No Direct Significance	In Baddy Waters Partial Libera- tion H ₂ S
Alkali Reserve (in Mg-equiv. l.)	1.6-2.5 (Ocean Water)	From 1.0 to 1.6 in the system range with From 60 to 180 Mg l. CO ₂ content	5.8-6.0	6.1	9.6-12.3

NOTE:

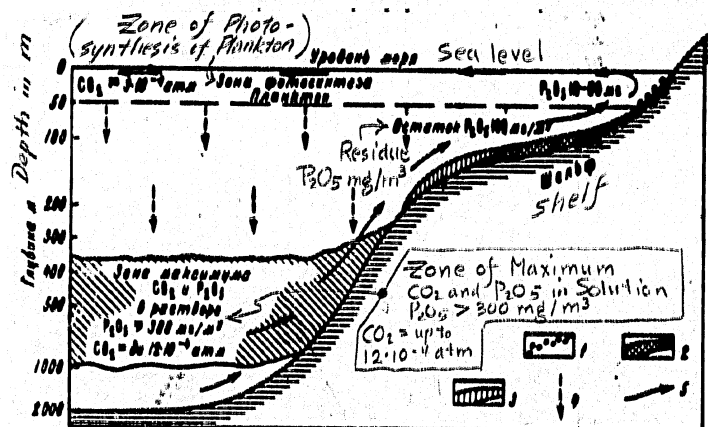
*
1) In Relation to a Hydrogen Electrode

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Figure 1. Diagram of the formation of the phosphate element of phosphate rocks as chemical marine deposits in the zone of the shelf under conditions of deep, cold, marine currents.

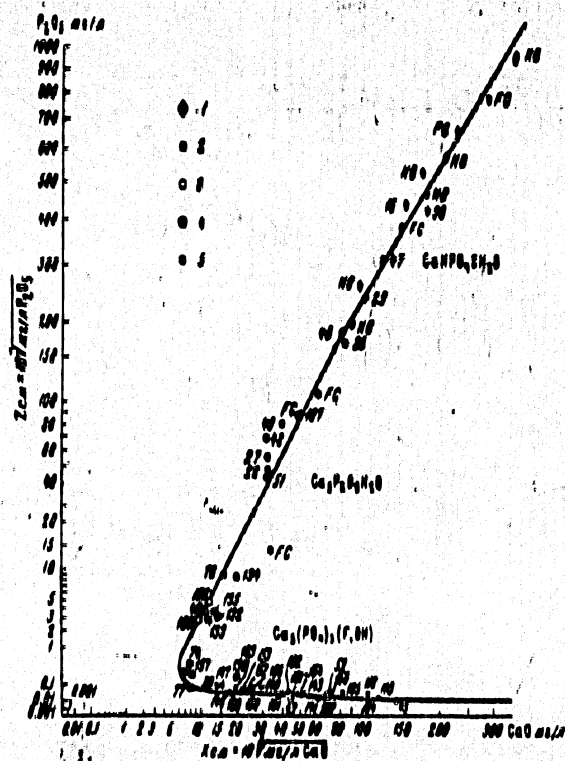
1. Phase of shore gravels and sands. 2. Phosphate phase. 3. Phase of argillaceous limestone deposits. 4. Falling of plankton remains. 5. Direction of currents.



Фиг. 1. Схема образования фосфатного вещества фосфоритов как морских химических осадков в зоне шельфа в условиях глубинных холодных морских течений.

1 - фаза береговых галечников и песков, 2 - фосфорная фаза, 3 - фаза глинисто-известковых осадков, 4 - падение остатков планктона, 5 - направление течений (see above)

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Фиг. 2. Система $\text{CaO} - \text{P}_2\text{O}_5 - \text{HF} - \text{H}_2\text{O}$. Изотерма 20°C .

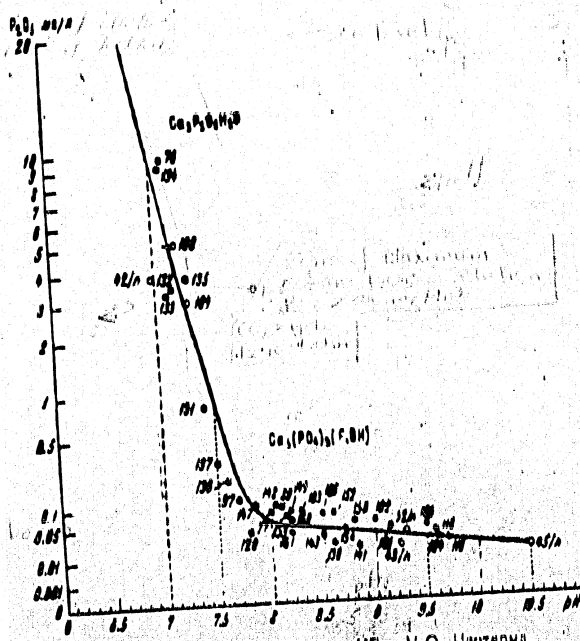
1 - моноклин, 2 - трикальций-фосфат, 3 - гидроксипатит,
4 - фтор-гидроксипатит, 5 - фтор-патит

Figure 2. System $\text{CaO} - \text{P}_2\text{O}_5 - \text{HF} - \text{H}_2\text{O}$. Isotherm 20 degrees Centigrade. 1. Monoclinic. 2. tricalcium-phosphate. 3. hydroxylapatite. 4. Fluor-hydroxylapatite. 5. Fluor-apatite.

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Figure 3. System $\text{CaO} - \text{P}_2\text{O}_5 - \text{HF} - \text{H}_2\text{O}$. Isotherm 20 degrees
 Continued. P_2O_5 f(pH) Symbols same as for Figure 2.



Фиг. 3. Система $\text{CaO} - \text{P}_2\text{O}_5 - \text{HF} - \text{H}_2\text{O}$. Изотерма
 20° Ц. P_2O_5 f(pH)
 Обозначения те же, что на Фиг. 2

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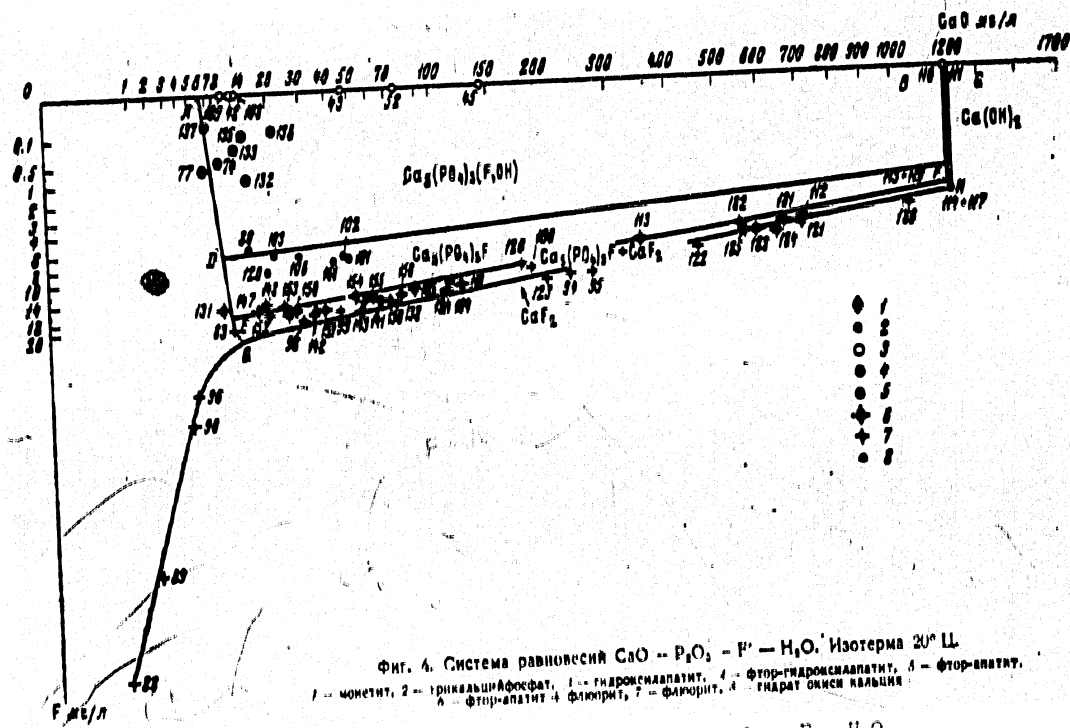


Figure 4. Scheme of equilibria $\text{CaO} - \text{P}_2\text{O}_5 - \text{F} - \text{H}_2\text{O}$.

Isotherm 20 degrees Centigrade. 1. monite 2. tricalcium-phosphate
3. hydroxylapatite 4. Fluor-hydroxylapatite 5. fluor-apatite
6. fluor-apatite plus fluorite 7. fluorite 8. calcium hydroxide

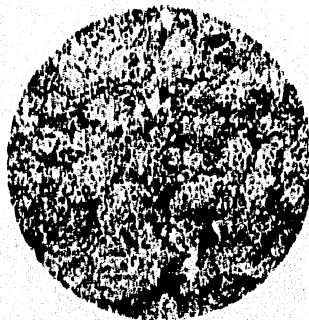
[Figures 5, 6, 7 illegible. See text.]

[Photographs showing typical 'stratified apatite', which had been converted from ordinary carbonate rocks (see top of page 2 in this translation)]

[see next page]

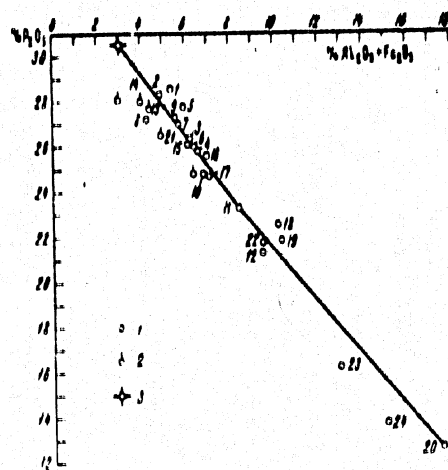
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[Figures 5, 6, 7]



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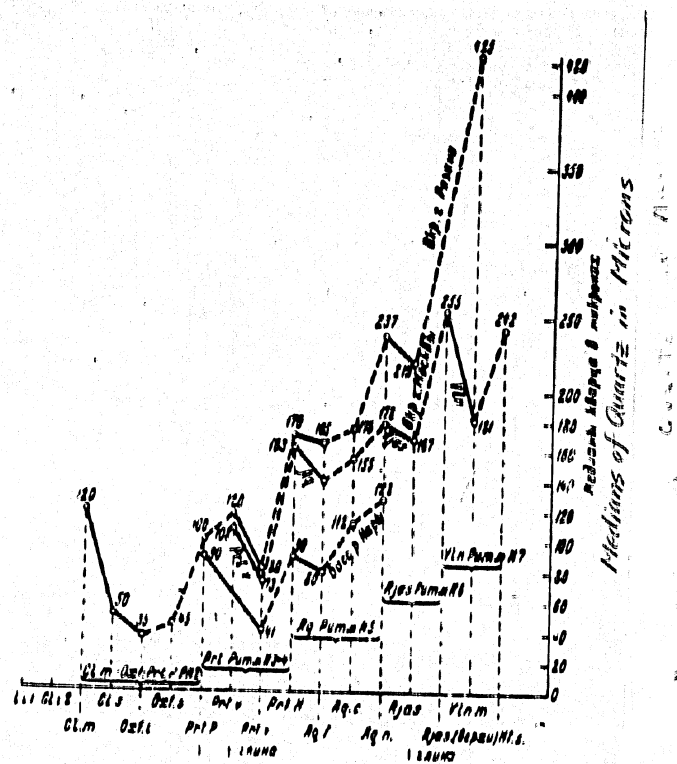
Figure 6. Correlative relationship of P_2O_5 and R_2O_3
for Upper Kansk phosphate rocks. 1. washing 2. float-concentrate
3. concentration limit



Фиг. 8. Коррелятивное соотношение P_2O_5 и R_2O_3 для
верхнеканских фосфоритов.
1 - мытый, 2 - флотконцентрат, 3 - предел обогащения

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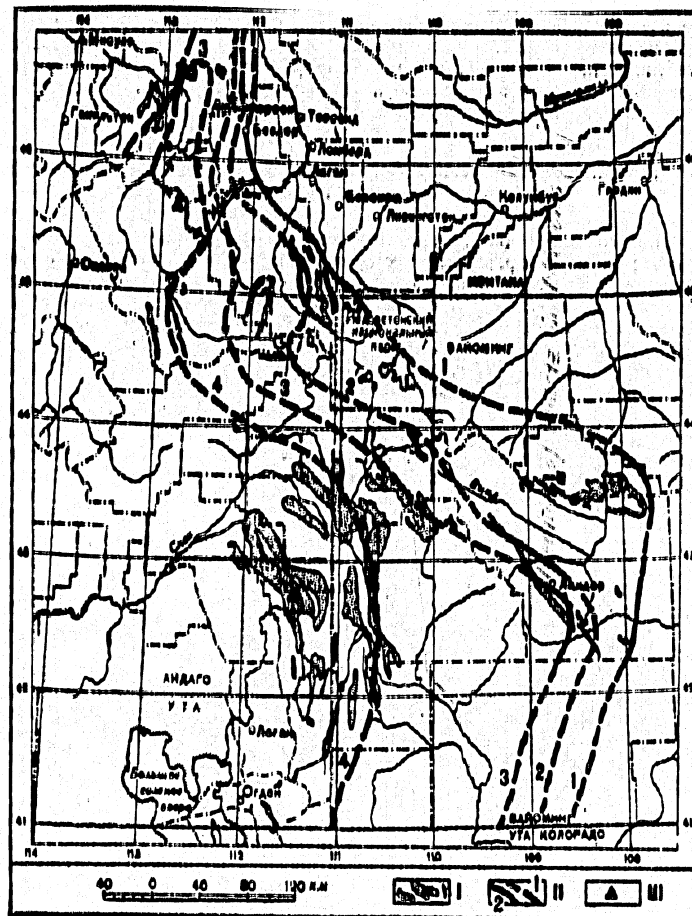
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Фиг. 9. Ритмограммы (эпетрограммы) мезозоя Подмосковного бассейна (по данным гранулометрии осадков). Сплошной чертой обозначена трансгрессия, прерывистой - регрессия.

Figure 9. Rhythmograms (epetrograms) of the Mesozoic of the Moscow region basin (according to data on the granulometry of the deposits). Solid line indicates transgression; broken -- regression.

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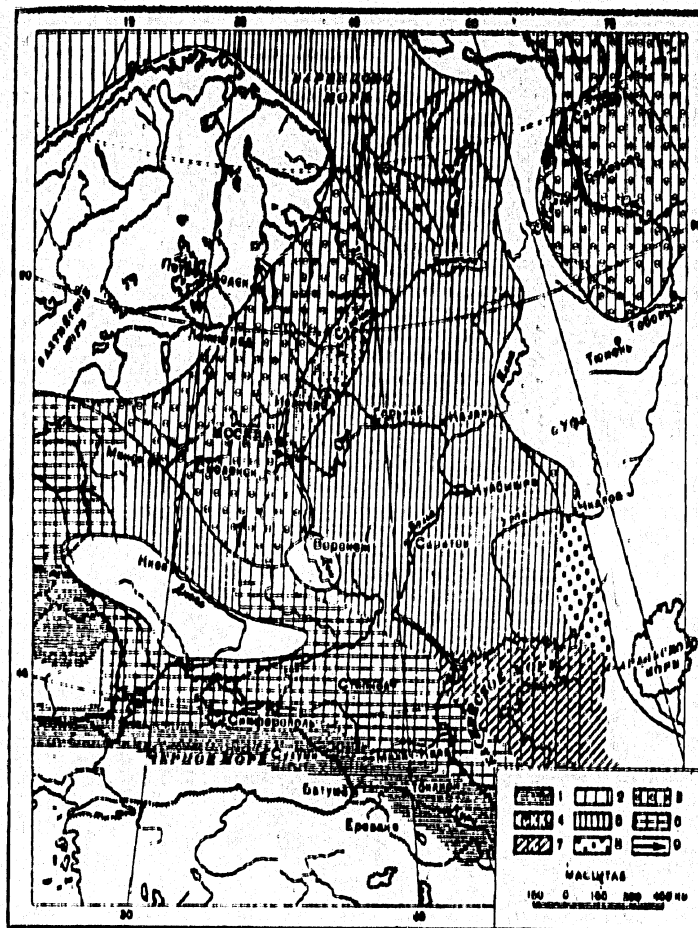


Фиг. 10. Карта фосфоритных полей западной части США
 I — известные или предполагаемые поля промышленных залежей; II — линии, указывающие ширину в футах главного фосфоритного слоя; III — фосфоритный рудник Анаконда

Figure 10. Map of phosphate rock fields in western US.

I. known or assumed fields of commercial deposits II. lines indicating width in feet of main phosphate rock strata III. Anaconda phosphate rock mine.

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Фиг. 11. Русская платформа в калловии и оксфорде (по А. Н. Мазаровичу)

1 — геосинклинальные бассейны, 2 — трансгрессии на платформе, 3 — области, захваченные морем в оксфорде, 4 — песчаные фации калловия, 5 — глинистые фации калловия, 6 — известняковая фация, 7 — известняково-марлевая фация, 8 — континентальные породы, 9 — направление трансгрессии

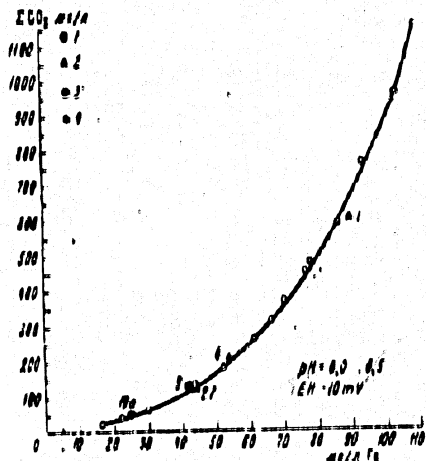
Figure 11. Russian platform in the Callovian and Oxford (ac-

cording to A. N. Mazarovich) 1. geosynclinal basins 2. transgressions on the platform 3. districts covered by the sea in the Oxford 4. sand phases of the Callovian 5. clay phases of the Callovian 6. limestone phase 7. limestone-marl phase 8. continental beds 9. direction of transgressions

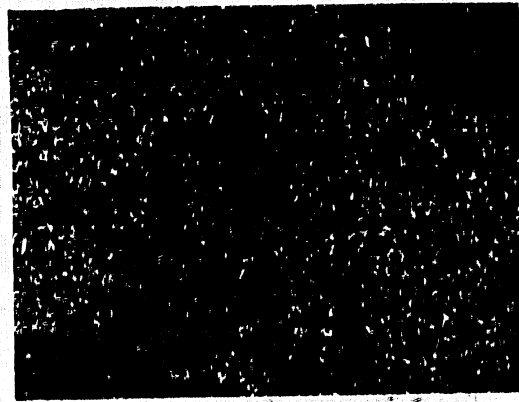
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Figure 12



Фиг. 12. Сидеритовая система $\text{FeO} - \text{CO}_2 - \text{H}_2\text{O}$.
Изохора 14, 20° II pH = 6.0 - 6.5, EH = 10 mV.
1. метод растворения Fe проволоки в системе $\text{H}_2\text{O} - \text{CO}_2$
2. метод кристаллизации FeCO_3 из системы $\text{FeO} - \text{CO}_2 - \text{H}_2\text{O}$
3. метод дегазификации с последующим вымачиванием в воде
4. эксперименты Тилемана и Клармана на метод растворения Fe
проволоки в системе $\text{H}_2\text{O} - \text{CO}_2$.



Фиг. 13. Синтетические идиоморфные ромбы доломита.
Увеличено в 240 раз. Опыт 72.
Тонкая фаза системы $\text{CaO} - \text{MgO} - \text{CO}_2 - \text{H}_2\text{O}$ 150° P = 5 atm

Figure 13

[see below, bottom of page]

Figure 12. Siderite system $\text{FeO} - \text{CO}_2 - \text{H}_2\text{O}$. Isotherm 14-20 degrees Centigrade. pH equals 6.0 ... 6.5. EH = 10 mV. 1. method of dissolving Fe wire in the system H_2O plus CO_2 2. method of crystallizing FeCO_3 out of the system $\text{FeO} - \text{CO}_2 - \text{H}_2\text{O}$ by means of degasification with subsequent soaking 3. method of dissolving synthetic amorphous FeCO_3 and Fe(OH) , in the system H_2O plus CO_2 4. experiments of Tilman and Klarman on the method of dissolving Fe wire in the system H_2O plus CO_2 .

[Figure 13 illegible]

Figure 13.

Synthetic idiomorphic rhombohedra of dolomite,
magnified 240 times. Experiment 72.

Bottom phase of the system: $\text{CaO} - \text{H}_2\text{O} - \text{CO}_2 - \text{H}_2\text{O}$,
 $T = 150^\circ$, $P = 5 \text{ atm}$.

[see Figure 13, top right]

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